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Effect of Oxidation on Mechanical Properties of Fibrous Monolith Si_3N_4/BN at Elevated Temperatures in Air

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The oxidation behavior and its effect on the mechanical properties of fibrous monolith Si_3N_4/BN after exposure to air at temperatures ranging from 1000° to 1400°C for up to 20 h were investigated. After exposure at 1000°C, only the BN cell boundary was oxidized, forming a B_2O_3 liquid phase. With increasing exposure temperature, the Si_3N_4 cells began to oxidize, forming crystalline $Y_2Si_2O_7$, SiO_2, and silicate glass. However, in this case, a weight loss was observed due to extensive vaporization of the B_2O_3 liquid. After exposure at 1400°C, large $Y_2Si_2O_7$ crystals with a glassy phase formed near the BN cell boundaries. The oxidation behavior significantly affected the mechanical properties of the fibrous monolith. The flexural strength and work-of-fracture decreased with increasing exposure temperature, while the noncatastrophic failure was maintained.

I. Introduction

Silicon nitride (Si_3N_4) based composites have been regarded as one of the most promising materials for high-temperature structural applications.[1–4] Among these, fibrous monolith Si_3N_4/boron nitride (BN), consisting of a hexagonal arrangement of strong Si_3N_4 cells surrounded by weak BN cell boundaries, has been found to exhibit noncatastrophic failure with high strength both at room temperature and at high temperatures due to extensive crack interactions (crack delaminations and crack deflections) through the BN cell boundaries.[4–7]

As this material was intended for use at high temperatures, the oxidation behavior is one of the more important criteria that need to be clearly understood before it can be applied. The oxidation resistance of Si_3N_4 containing sintering aids is strongly influenced by the composition and crystalline state of the secondary phase.[8–12] However, when BN is exposed to an oxidizing atmosphere above 1000°C, it reacts with oxygen, forming a B_2O_3 liquid or a gas phase.[13] Such oxidation behavior strongly affects the mechanical properties of the materials by forming an oxide scale on the surface.[12]

In this paper, the oxidation behavior of a fibrous monolith in air at temperatures between 1000° and 1400°C was investigated. The oxidation behavior was measured by monitoring the weight changes of the specimens. The oxidation products that formed on the surface were identified by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). In addition, the mechanical properties, such as the strength and work-of-fracture (WOF), were measured using four-point bending tests and related to crack propagations.

II. Experimental Procedure

Fibrous monolith Si_3N_4/BN was fabricated by hot pressing using a method described elsewhere.[5] Sintered billets were cut into dimensions of 2 mm × 4 mm × 10 mm to measure the weight changes, and were machined with a 600-grit diamond wheel, and subsequently polished down to 3 μm with a resin-bonded diamond wheel. Specimens with dimensions of 3 mm × 4 mm × 50 mm were prepared for the mechanical tests using a similar methodology. The tensile surface was polished down to 3 μm and slightly chamfered to remove the existing defects. In addition, the side surfaces of each specimen were polished down to 30 μm.

Before oxidation, the surfaces were ultrasonically cleaned in acetone and ethanol. The oxidation test was conducted in a vertical alumina tube-furnace at temperatures ranging from 1000° to 1400°C for 20 h in laboratory air. The furnace was heated at a heating rate of 10°C/min and maintained at the exposure temperatures. The polished specimens, suspended at the end of a platinum wire, were inserted into the hot zone from the top. Such a rapid heating process was selected to minimize oxidation during the heating stage, while a furnace cooling process was used to minimize the thermal stress. The weights of each sample were measured both before and after exposure using a digital balance with an accuracy of 0.1 mg. The oxidized surfaces were examined by SEM, XRD, and EDS. The flexural strength and apparent work-of-fracture were measured using a four-point flexural configuration with inner and outer spans of 20 and 40 mm, respectively, at a crosshead speed of 0.5 mm/min. In addition, crack propagation after the bending test was examined by optical microscopy.

III. Results and Discussion

The oxidation behavior was analyzed by monitoring the weight change of the specimens exposed to air between 1000° and 1400°C for up to 20 h, as shown in Fig. 1. When the specimens were exposed at 1000°C, the weight changes were found to be a function of the exposure time. At an early stage of oxidation, a weight gain was observed, implying that $B_2O_3(l)$ was formed on the cell boundary. However, as the exposure time was increased, a weight loss was observed as a result of $B_2O_3(l)$ vaporization. As the exposure temperature was increased to 1200°C, the $B_2O_3(l)$ vaporization became more

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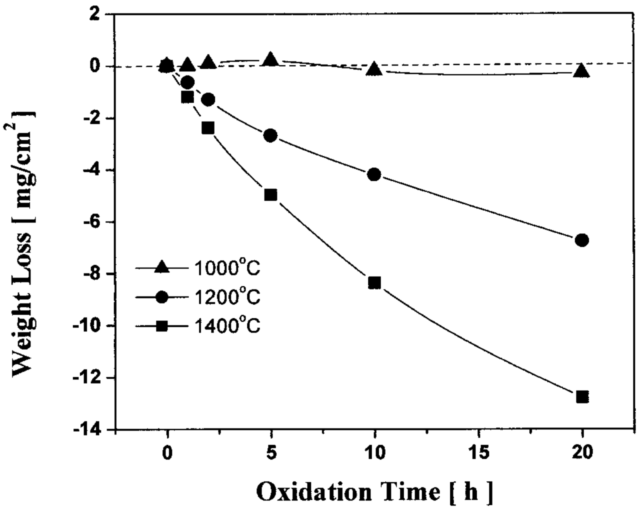

Fig. 1. Weight changes of the samples exposed to air at temperatures between 1000° and 1400°C for up to 20 h.

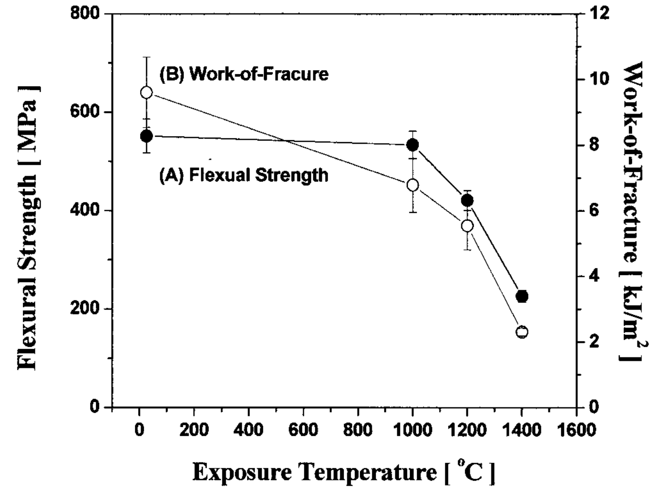

Fig. 3. (A) Flexural strength and (B) work-of-fracture of the sample as a function of the exposure temperature.

vigorous, leading to an extensive weight loss. However, at this temperature, the Si_3N_4 cells began to oxidize, forming crystalline $Y_2Si_2O_7$, SiO_2 (cristobalite), and a glassy phase. At higher exposure temperatures (1400°C), the weight loss became more pronounced even though the Si_3N_4 was oxidizing to a greater extent. Therefore, the observed weight loss was mainly caused by BN oxidation, indicating that the kinetic constant for BN oxidation is much higher than that of Si_3N_4.

Oxidized surfaces after the different exposure temperatures are shown in Figs. 2(A) and (B). Hot-pressed fibrous monolith consists of ~250 μm cells of composition Si_3N_4 separated by 15–25 μm boron nitride cell boundaries. After exposure at 1000°C for 20 h, the surface morphology had changed relatively little. That is, the cell boundary was slightly damaged, revealing a B_2O_3 liquid phase with platelike BN. As the exposure temperature was increased to 1200°C, the BN cell boundary was severely damaged because of extensive oxidation, leaving a large amount of a glassy phase without the platelike BN, as shown in Fig. 2(A). In addition, needlelike $Y_2Si_2O_7$ crystals, confirmed by EDS, which were embedded in the glassy phase, formed in the Si_3N_4 cell region. At 1400°C, the Si_3N_4 cells were also severely damaged, revealing an oxide layer composed of large $Y_2Si_2O_7$ crystals and a glassy phase, as shown in Fig. 2(B). The surface cracks were due to crystallization of a glassy phase on cooling. However, the BN cell boundary layers were completely covered by oxidation products.

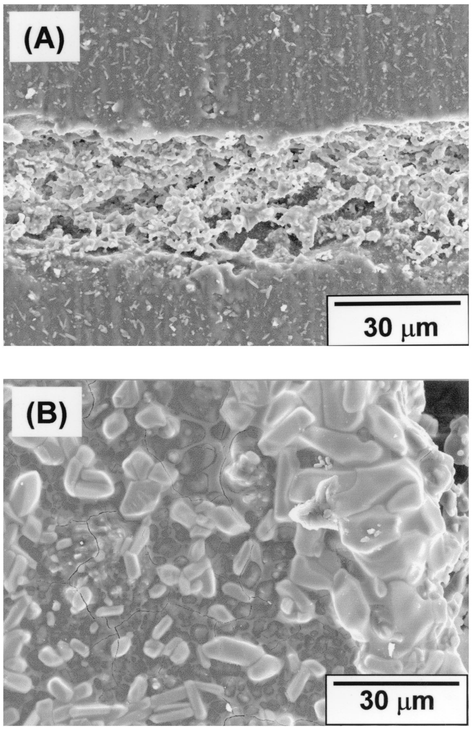

Fig. 2. SEM micrographs of the samples exposed to air for 20 h at (A) 1200° and (B) 1400°C.

Before oxidation, the fibrous monolith exhibited noncatastrophic failure due to extensive crack interactions through weak BN cell boundaries. This leads to a high WOF (9.6 ± 1.1 kJ/m^2) and a high strength (551 ± 34 MPa). Noncatastrophic failure was observed after oxidation, regardless of the exposure temperature. However, with increasing exposure temperature, the maximum apparent strength and crack interactions decreased, which was apparently due to degradation of the cell boundary layers. The flexural strength and WOF of the fibrous monolith after oxidation at the different temperatures are shown in Fig. 3. When the sample was exposed to air at 1000°C for 20 h, the reduction in flexural strength was negligible. However, the WOF decreased because of the reduction in the crack interactions with the cell boundaries. At higher exposure temperatures, both the flexural strength and the WOF decreased. However, even after exposure to air at 1400°C for 20 h, the sample maintained 41% (~226 MPa) and 21% (~2.3 kJ/m^2) of its initial strength and WOF, respectively.

The changes in the mechanical properties are related to the interactions of cracks with the weak BN cell boundaries, as shown in Figs. 4(A–C). When the sample was exposed to air at 1000°C, the sample showed extensive crack interactions with the weak BN cell boundaries, which suggest that the surface layer was not severely damaged (Fig. 4 (A)). With further increases in the exposure temperature to 1200°C, the BN cell boundaries were severely damaged because of $B_2O_3(l)$ vaporization. However, extensive crack interactions were also observed (Fig. 4(B)). Therefore, the reduced WOF was mainly due to a reduction in strength retention before the surface fracture. This implies that a high WOF can be achieved when the sample retains a high strength before the first failure with significant crack interactions. At the highest exposure temperature (1400°C), the surface layer was surrounded by a thick oxide layer as a result of Si_3N_4 and BN oxidation, leading to a lower number of crack interactions, as shown in Fig. 4(C). However, significant crack interactions were still observed in the load versus the deflection curve during the bending test because the inner part was not damaged extensively by the exposure.

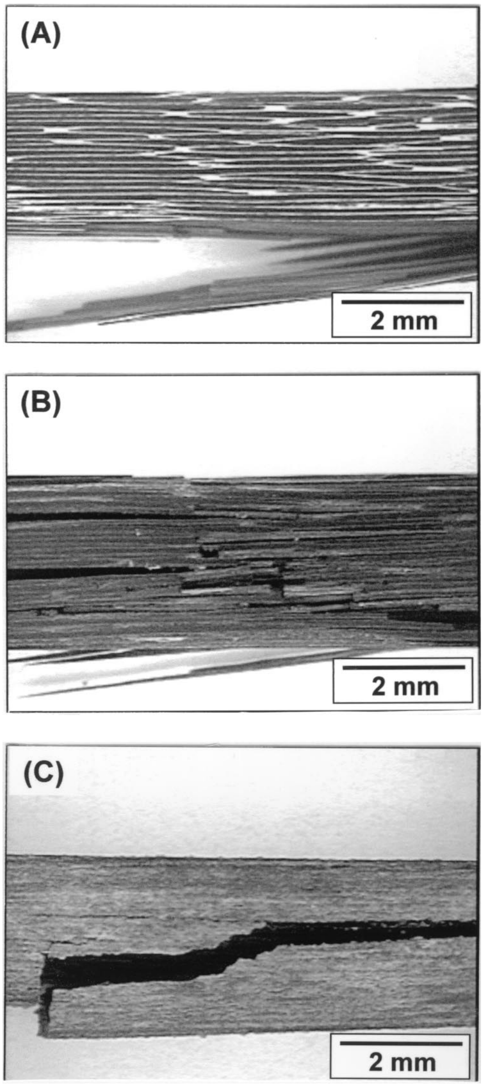

Fig. 4. Optical micrographs of the crack propagations in the sample during the bending tests after exposure to air for 20 h at (A) 1000°, (B) 1200°, and (C) 1400°C.

IV. Summary and Conclusions

The oxidation behavior of fibrous monolith Si_3N_4/BN was investigated and correlated with the changes in the mechanical properties after exposure to air at temperatures ranging from 1000° to 1400°C for up to 20 h. As the exposure temperature was increased, the B_2O_3 liquid vaporized rapidly, leading to an overall weight loss. However, Si_3N_4 was oxidized at above 1200°C, leaving $Y_2Si_2O_7$ crystals surrounded by a glassy phase. These oxidized surfaces strongly affected the mechanical properties of the fibrous monolith. As the exposure temperature was further increased, the flexural strength and WOF decreased, while the noncatastrophic failure was maintained.

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